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(54) Laminated preform with internal barrier layer.

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Description

This invention relates to a method of forming a laminated preform according to the preamble of claim 1. Such a method is known from DE-A-2445112 (equivalent to US-A-3976226).

Currently multi-layer containers are produced commercially utilizing the following methods of processing:

a. Coextrusion blow molding
b. Coextrusion stretch blow molding
c. Tube coextrusion and reheat stretch blow molding
d. Sequential injection molding of preforms in multi-station injection molds and stretch blow molding.

Among the methods listed above, method "d" is the only one which yields finished cold multi-layer preforms. But this method is still not practical for producing multi-layer preforms with one of the layers having a thickness of .076mm to .38 mm (.003 to .015 inch) There has been developed a method of forming a preform by injection molding wherein there is incorporated therein a central layer of barrier material. This is disclosed in U.K. patent application No. 2091629A. However, because of the cost of the barrier material, the thickness of the barrier layer which is possible in accordance with that patent application is too great to be commercially feasible.

Barrier materials which are suitable for use in the forming of containers have 2 to 3 magnitudes higher gas barrier and are 4 to 8 times more expensive when compared to thermoplastic materials suitable for use in the forming of containers. The thickness of the barrier layer required in a container wall for the majority of the packaging applications is on the order of .0127mm to .038mm (.0005 to .0015 inch). This would, assuming a 10 times wall thickness reduction during the biaxial orientation of blow molding a preform, translate to a .127mm to .38mm (.005 to .015 inch) layer thickness of the barrier material in the wall of a multi-layer preform.

DE-A-2445112 discloses an apparatus for the manufacture by injection molding of articles composed of a plurality of layers of at least three distinct materials coated one over the other, in which there is injected a measured quantity of a first material adapted to form the skin of the article, a measured quantity of a second material to form the intermediate layer, and a measured quantity of a third material to form the body of the article, The materials are introduced to the mold coaxially so as to give a uniform distribution. The injection-molding apparatus includes an injection nozzle having a single discharge channel opening on the side of the mold and at least three coaxial chambers each connected to a separate supply circuit for each material to be injected. However, this specification does not disclose any way in which the thickness of the barrier material can be reduced to a minimum.

Accordingly, the present invention provides a method of forming a laminated preform of the type including an intermediate layer, the method comprising the steps of:

providing an injection mold (20) for said preform wherein the injection mold (20) includes a core (24) with there being a cavity (22) surrounding the core, providing separate supplies of at least one first flowable thermoplastic resin (56, 72) adapted to form the skin of the preform and a second flowable material (66),

injecting into that end of said mold cavity which defines a preform bottom a limited quantity of said first thermoplastic resin (56) with the surface portions of said limited quantity of thermoplastic resin coming into contact with said mold (20) and said core (26),

injecting a limited quantity of said second material (66) into said mold cavity behind said limited quantity of first thermoplastic resin for forming said at least one intermediate layer with said second material forcing said first thermoplastic resin further into said cavity with said second material having tunnel flow within said thermoplastic re;sin with surface portions of said second material in contact with said first thermoplastic resin,

and then injecting other flowable thermoplastic resin (72) into said mold cavity (22) behind said second material (66) sufficient to complete filling of said mold cavity with said other flowable thermoplastic resin forcing said limited quantities of said first thermoplastic resin (56) and said second material (66) to flow toward the other end of said mold cavity (22), and permitting all of the injected material to solidify, characterised in that said second flowable material (66) is a barrier material, in that the surface portions of said limited quantity of thermoplastic resin cool due to contact with said mold (20) and said core (26) to define first solidified layers (58, 60) while there is tunnel flow of the thermoplastic resin between said solidified layers, in that surface portions of said second, barrier material in contact with said first thermoplastic resin cool and form second solidified layers (68, 70), and wherein said barrier material (66) has a melting temperature lower than that of said other thermoplastic resin (72) with said other thermoplastic resin as it flows between the layers (68, 70) of barrier material heating contacted layers of said barrier material and forcing portions thereof forwardly into said mold cavity (22) thereby to effect thinning of the layers of barrier material.

In accordance with this invention, one takes

advantage of mold filling phenomenon which comprises:

1. Laminar flow
2. The development of elongational and shear fields in the advancing melt front between two parallel cold walls
3. The formation of oriented solidified layers on the cold wall and the tunnel flow of molten material between the solidified layers.

A feature of this invention is the ability to provide two very thin barrier Layers instead of one thick layer and the advantages resulting therefrom.

The present invention is further described hereinafter, by way of example, with reference to the accompanying drawings, in which:

IN THE DRAWINGS:

Figure 1 is a schematic sectional view taken through one injection mold cavity, and shows the manner in which material is directed into the cavity to form a preform in accordance with this invention.

Figure 2 is an enlarged fragmentary schematic view showing the manner in which a first quantity of thermoplastic resin is injected into the bottom of the mold cavity and the resultant cooling upon contact with cold wall surfaces.

Figure 3 is a schematic sectional view similar to Figure 2, and shows the injection of a barrier material into the bottom of the mold cavity and the resultant tunnel flow of both the first quantity of thermoplastic resin and the barrier material.

Figure 4 is a schematic fragmentary sectional view similar to Figures 2 and 3, and shows the progressive flow of a second quantity of thermoplastic resin into and through the layers of the first thermoplastic resin and the barrier material.

Figure 5 is an enlarged fragmentary radial sectional view showing the flow of the thermoplastic material forming the first layers of the laminated preform.

Figure 6 is a diagram plotting the injection of the materials into the mold cavity against time.

Figure 7 is another diagram plotting pressure within the mold cavity against time.

Figure 8 is an enlarged radial sectional view through the neck finish end of a preform in accordance with this invention for forming a blow molded bottle, and shows one arrangement of material layers within the preform.

Figure 9 is a fragmentary sectional view similar to Figure 8, but showing another relationship of the material layers in the area of the neck finish.

Figure 10 is yet another enlarged fragmentary sectional view similar to Figure 8, and shows yet another arrangement of the material layers within the preform.

Figure 11 is an enlarged fragmentary sectional view similar to Figure 8, but through a slightly different type of preform, and shows the arrangement of the layers therein.

Figure 12 is yet another enlarged fragmentary sectional view similar to Figure 8, but with respect to a preform of the type shown in Figure 11 and showing yet another arrangement of material layers.

Figure 13 is a vertical sectional view taken through an intermediate article of manufacture utilizing a preform such as that shown in Figures 11 and 12.

Figure 14 is a fragmentary enlarged radial sectional view taken generally along the line 14-14 of Figure 13, and shows the arrangement of the layers of material within the article.

Figure 15 is an enlarged fragmentary sectional view similar to Figure 14, and shows a different arrangement of the material layers.

Figure 16 is a vertical sectional view taken through a bottle or like container formed utilizing one of the preforms of Figures 8-10.

Figure 17 is an enlarged fragmentary radial sectional view taken generally along the line 17-17 of Figure 16, and shows the relationship of layers of material in the finished bottle.

Referring now to the drawings in detail, it will be seen that there is illustrated in Figure 1 a conventional injection mold generally identified by the numeral 20. It is to be understood that this is a schematic showing in that a conventional injection mold for forming a preform will include numerous cavities, for example sixteen or more, arranged in rows and columns. Such an injection mold is generally of a solid construction and each injection mold unit will include a mold cavity 22. Each mold unit 20 will also include a neck ring 24 which forms an extension of the mold cavity 22 and defines a neck finish. The neck ring 24 may be of a split construction. Further, each mold unit 20 is provided with a core 26.

It will be seen that the neck ring 24 in conjunction with the core 26 closes what may be considered to be the upper end of the mold cavity 22 while the lower end of the mold cavity is provided with an opening 28 which may receive in sealed relation the nozzle of an extruder.

In accordance with the present invention, in lieu of the nozzle of the extruder being directly received within the opening 28, a nozzle-like end 30 of a rotary valve member 32 is received in the opening 28 in sealed relation. The valve member 32 is mounted in sealed relation within a valve block 34 which has formed therein a first passage 36 which receives the conventional nozzle 40 of a plasticizer or injection head. The passage 36 opens radially toward the rotary valve member 32. The rotary valve member 32 has a through passage 42

which at one end terminates in a generally radial passage 44 which can be aligned with the passage 36. There is also associated with the valve block 34 a second material dispenser 46 which in its simplest form may include a dispensing piston 48 and which has a flow passage 50 exiting therefrom toward the valve block 34. The valve block 34 has a radial passage 52 which is axially aligned with and in communication with the passage 50. The passage 52 terminates at the valve member 32. The valve member 32 has a further passage 54 extending generally radially from the passage 42 and so circumferentially spaced from the passage 44 such that when the passage 44 is aligned with the passage 36 the passage 54 is spaced from the passage 52 in a circumferential direction. By rotating the valve member 32, the passage 44 may be moved out of communication with the passage 36 and the passage 54 moved into communication with the passage 52. Thus material may be selectively supplied from either the plasticizer or from the supply device 46.

In accordance with this invention, the material delivered by the plasticizer will be a suitable thermoplastic resin in the form of a hot melt. This resin may be such materials as PET, PP, PE, PVC and PC. The barrier material which is supplied by the supply device 46 may be of any conventional known barrier material including, for example, EVAL, EVOH, PVOH and the like, or such barrier materials as may be developed in the future.

With respect to the foregoing, it is to be noted that EVAL has barrier properties on the order of one hundred times that of PET; EVOH has barrier properties on the order of one hundred to two hundred times that of PET: and PVOH has barrier properties on the order of two thousand times that of PET. Accordingly, only a very thin layer of these barrier materials is required, and from a commercial standpoint it is highly desireable to maintain such very thin layers because of the much higher cost of the barrier materials than the acceptable thermoplastic resins including PET.

It is also to be understood that the external thermoplastic resin layers must be of sufficient thickness to protect the barrier layer. On the other hand, in the case of a bottle for beverages or other products containing CO_2, the innermost layer of the thermoplastic material, i.e. that which defines the interior of the container, must be relatively thin so as not to absorb CO_2.

With the foregoing requirements in mind, the manner in which a laminated preform is formed in accordance with this invention will be described in detail.

Referring first to Figure 2, it will be seen that a preselected limited amount of a first thermoplastic resin 56 will be injected into the bottom of the mold cavity 22 and as it flows through the mold cavity, due to the relatively cool temperature of the mold unit 20 including the core 26, there will be solidification of the thermoplastic resin 56 both externally and internally of the mold cavity 22 to define inner and outer layers 58, 60 of the first thermoplastic resin.

Reference is particularly made to Figure 5 at this time wherein it will be seen that the thermoplastic resin 56 has a laminar flow with the velocity of the advancing thermoplastic resin being the greatest in the center and diminishing toward zero adjacent the mold components. The velocity of the advancing thermoplastic resin 56 is generally indicated by an arrow schematic arrangement 62. It is to be understood that as the thermoplastic resin 56 solidifies upon contacting the mold components, the flow of the thermoplastic resin will discontinue adjacent the walls of the mold cavity 22 and there will be a tunnel flow effect between the layers 58, 60. Further, due to the relatively cool air within the mold cavity 22, there will be a slight cooling of the advancing front of the thermoplastic resin 56, which front is identified by the numeral 64.

It is to be understood that the thickness of the layers 56, 60 will be varied depending upon factors such as:

1. Material properties (viscoelastic and thermal)
2. Cavity dimensions
3. Injection velocity (pressure).

It is to be understood that a precise amount of the first thermoplastic resin 56 will be injected into the mold cavity 22 over a selected period of time, with this being schematically shown in Figure 6, and at a low pressure as indicated in Figure 7. The quantity of the thermoplastic resin which is injected into the mold cavity may be controlled in many conventional manners. Basically, injection of the thermoplastic resin is effected by axially advancing the feed screw of a plasticizer, and a suitable stop may be provided to limit the advance of the feed screw. There also will be the timed rotation of the valve member 32 to move the passage 44 out of alignment with the passage 36 and thus the quantity of thermoplastic resin 56 injected into the mold cavity 22 may be controlled by the timing of the actuation of the valve member 32.

As is schematically shown in Figure 6, the barrier material which is next injected into the mold cavity and is identified by the numeral 66, is fed toward the mold cavity in slightly overlapping relation with respect to the thermoplastic resin 56. It is to be understood that mechanism for feeding the barrier material 66, as schematically shown in Figure 1, may be of a single shot type so as to inject the exact amount of barrier material required.

With respect to Figure 7, it will be seen that the barrier material 66 will be injected into the mold

cavity 22 ay a pressure only slightly higher than the pressure of the thermoplastic resin 56 with there being a very slight pressure drop as at 67 between the discontinuation of injecting the thermoplastic resin 56 and the initiation of the injection of the barrier material 66. The overlap in injection is to keep the pressure drop to a minimum.

Referring now to Figure 3, it will be seen that the barrier material 66 will have a tunnel flow through the cavity defined between the layers 58, 60 and at the same time will advance the previously injected thermoplastic material 56. Normally the barrier material will have a lower melting temperature than the thermoplastic resin 56, and therefore the cooling effect of the thermoplastic resin layers 58, 60 on the barrier material 66 will not be as great as the mold surfaces on the thermoplastic material 56. Thus, while there will be a solidification of the barrier material 66 as it contacts the solidified layers 58, 60 and there will be formed inner and outer solidified layers 68, 70 of the barrier material, these layers will be materially thinner than the layers 58, 60. For example, the layers 58, 60 will have a thickness varying from .254mm to 1.02mm (.010 to .040 inch), while the barrier material layers 68,70 will have a thickness as low as .076mm (.003 inch).

Referring now to Figure 4, in the illustrated embodiment of the mechanism for feeding the thermoplastic resin, an additional supply of the same thermoplastic resin identified by the numeral 56 is injected into the mold cavity. This additional supply of thermoplastic resin is generally identified by the numeral 72. The thermoplastic resin 72 as it advances within the confines of the layers 68, 70 of the barrier material will re-melt the barrier material and advance it together with the barrier material melt 66 through the tunnel defined by the layers 68, 70, thereby reducing the thickness of the layers 68, 70. As will be apparent from Figure 4, the advancing thermoplastic resin 72 will advance the barrier material 66 which, in turn, will continue to advance the thermoplastic resin 56.

Further with respect to Figure 4, it will be seen that the advancing large quantity of the thermoplastic resin 72 as it engages the layers 58, 68 at the end of the core 26, will melt portions of the solidified layers 58, 68 and advance the same with the result that there may be no portion of either the layer 58 or the layer 68 at the extreme end of the core 26.

Referring next to Figure 6, it will be seen that the thermoplastic resin 72 is advanced in slightly overlapping relation with the barrier material 66. It is to be understood that once the injection of the barrier material 66 has been completed the valve member 32 will be rotated to a position to receive the thermoplastic resin 72. In the illustrated embodiment, the valve member 32 will be returned to its starting position since the thermoplastic resin 72 is delivered from the same supply as the thermoplastic resin 56.

With respect to the diagram of Figure 7, it will be seen that the thermoplastic resin 72 will be injected first at a gradually increasing pressure above the pressure of the injection of the barrier material 66 with a slight initial pressure drop, as indicated at 74. Then, when the cavity 22 has been filled, there will be a pressure boost, as at 76, followed by a holding period 78 wherein the pressure of the hot melt material injected into the mold cavity will gradually decrease as the thermoplastic material 72 gradually solidifies.

Depending upon usage of the preform which is formed in the manner described above, the amount of the thermoplastic resin 56 and the barrier material 66 injected into the mold cavity 22 will vary. Further, the shape of the preform at the front end thereof will vary.

In Figures 8, 9 and 10, there are illustrated preforms which are particularly adapted to be used in their entireties in the blow molding of bottles and like containers wherein a small diameter closure is applied by means of screw threads.

With respect to Figure 8, the illustrated preform portion is part of a preform identified by the numeral 80 and includes a laminated body 82 which terminates in a neck finish generally identified by the numeral 84. The neck finish 84 includes injection molded threads 86 and a shoulder member 88 by means of which the preform 80 is supported during reheating and blow molding.

In the preform 80, the quantity of thermoplastic resin 56 injected into the mold cavity is sufficient to have the layers 58, 60 extend to the extreme end of the preform 80 and to form at the extreme end an end wall 59. Further, the quantity of barrier material injected into the mold cavity is sufficient to have the layers 68, 70 extend to a point adjacent the extreme end of the preform and to form an end wall 69 adjacent the end wall 59. The thermoplastic resin 72 will also extend to a point adjacent the extreme end of the preform 80 as permitted by the end wall 69.

In Figure 9 there is illustrated a preform 90 which will be of the same configuration as the preform 80. Further while the quantity of the thermoplastic resin 56 directed into the mold cavity will be sufficient for the layers 58,60 to go to the extreme end of the preform including a neck finish portion 92 thereof and to form the end wall, the quantity of the barrier material 66 injected into the mold cavity will be such that the layers 68, 70 will terminate interiorly of the preform short of the neck finish 92 into that area of the resultant bottle which becomes the shoulder of the bottle, as will be

described in detail hereinafter.

With respect to Figure 10, the preform 94 thereof is also of an identical configuration to the preform 80. However, the quantity of the thermoplastic resin 56 introduced into the mold cavity will be only sufficient for the layers 58, 60 to extend to a point adjacent to the neck finish 96 of the preform 94. Thus, the neck finish part of the preform 94 will be formed solely by the thermoplastic resin 72. Further, the quantity of the barrier material 66 injected into the mold cavity will be such that the layers 68, 70 terminate internally of the preform short of the termination of the layers 58, 60.

In Figures 11 and 12 there are illustrated preforms for forming containers and like hollow articles other than bottles or containers with small diameter neck finishes. An extreme end portion only in radial section of such preform is illustrated in each of Figures 11 and 12.

With particular reference to Figure 11, it will be seen that there is illustrated a preform 98 having an open end portion 100 which may include a supporting flange or collar 102. Inasmuch as the end portion 100, as will be described in detail hereinafter, is utilized solely as a support in the blow molding of the preform 98 into a tubular shape, it is not necessary that the barrier material 66 extend into the end portion 100. Therefore, only sufficient barrier material is injected into the mold cavity of the preform 98 so as to permit the layers 68, 70 to terminate adjacent the end portion 100. In a like manner, the quantity of thermoplastic resin 56 injected into the mold cavity will be only sufficient to have the layers 58, 60 extend generally into the area of the end portion 100. Thus, the end portion 100 will be formed entirely by the thermoplastic resin 72.

In Figure 12 there is illustrated yet another preform 104 which is identical to the preform 98 including an end portion 106 and a flange or collar 108, except that the end portion 106 is formed entirely by the thermoplastic resin 56 and the layers formed by the resins 66 and 72 terminate in relatively great spaced relation to the end portion 106. The preform 104 is advantageous in forming a container or like tubular body wherein an intermediate article of manufacture is involved.

Referring now to Figure 13, it will be seen that there is illustrated an intermediate article of manufacture generally identified by the numeral 110 and blow molded from a preform such as the preform 98 or the preform 104. The intermediate article of manufacture includes a base portion 112 in the form of a container. The base portion 112 includes a tubular body 114 having an integral bottom 116 and terminating in a closure receiving portion 118. The illustrated closure receiving portion 118 is in the form of a flange adapted to be engaged by a conventional metal end unit and forming part of a conventional double seam securing the metal end unit (not shown) to the base portion 112 which, when separated from the remainder of the intermediate article of manufacture 110, becomes a container.

Although it has not been so illustrated, the intermediate article of manufacture 110 may have the closure receiving portion 118 in the form of a neck finish which may be threaded or otherwise modified to receive a closure unit. At this time it is to be understood that except for the fact that it is formed from a laminated preform the intermediate article of manufacture 110 has been formed prior to this invention.

It will be seen that the intermediate article of manufacture also includes an upper blow molded portion 120 which terminates in an end portion 122 which will correspond to the end portions 100, 106 of the preform 98, 104.

With respect to Figure 14, the intermediate article of manufacture illustrated therein was formed from a preform such as the preform 104 of Figure 12. It is to be understood that the upper portion 120 is to be separated from the base portion 112 by a cutting action, such as a fusion cutting action, with the removal of a portion 124. It will be seen that in this embodiment of the invention the layers 68, 70 terminate in the closure receiving portion 118 and that the layer formed by the thermoplastic material 72 terminates entirely within the base portion 112. Thus all of the intermediate article of manufacture 110 which is to be severed from the base portion 112 will be formed by the thermoplastic resin 56 and may be reconditioned and reused.

On the other hand, with respect to Figure 15, there may be occasions where it is desired that the barrier material layers 68, 70 extend beyond the closure receiving portion 118 into the upper portion 120. Thus, when the base portion 112 is removed from the remainder of the intermediate article of manufacture 110, the layers 68, 70 of the barrier material will extend through the cut edge of the base portion 112 into the upper portion 120. In a like manner, the layers 58, 60 of the first thermoplastic resin will also extend into the upper portion 120. Thus, when the base portion 112 is severed from the remainder of the intermediate article of manufacture 110 by removal of the material in the area 126, the intermediate article of manufacture 110 illustrated in Figure 15 may be formed, for example, from the preform of Figure 11. When the cutting action involves heat fusion of the cut layers to one another may be effected at the end of the base portion 120.

In Figure 16 there is illustrated a conventional

bottle which may be formed from any one of the preforms of Figures 8, 9 and 10. The bottle is generally identified by the numeral 128 and includes a tubular body 130 having an integral bottom 132. The body 130 at its upper end is connected by way of a shoulder 134 to a neck finish 136.

It is to be understood that the neck finish 136 will be identical to the neck finish of the respective preform from which the bottle 128 is blow molded. Further, it will be seen that the termination of the layers 68, 70 of the barrier material may be at the extreme end of the neck finish 136 when the preform of Figure 8 is utilized. On the other hand, when the preform of Figure 9 is utilized, the layers 68, 70 of the barrier material will terminate in the shoulder 134 adjacent the neck finish 136. Finally with respect to the use of the preform of Figure 10, both the layers 68, 70 of the barrier material and the layers 58, 60 of the first thermoplastic resin will terminate in the shoulder 134 adjacent the neck finish 136.

With particular reference to the bottle 128, it is to be understood that in the normal blow molding of such bottle the body portion 130 will be very thin, having been reduced in thickness on the order of one-tenth or less so that the material forming the body 130 will have a positive and desired biaxial orientation. On the other hand, the material of the bottle 128 in the shoulder 134 closely adjacent the neck finish 136 will have only a minor reduction in thickness while the material in the neck finish 136 will not be reduced in thickness at all. Thus the barrier material 66 may beneficially terminate in the shoulder 134 as described above.

It is also pointed out here that the extreme center of the bottom 132 is of a much greater thickness than the body 130, and therefore the absence of barrier material in the central part of the bottom 132 will not be a material omission.

Reference is finally made to Figure 17 which is a radial cross section of the body 130 and shows inner and outer layers 58, 60 of the first thermoplastic material 56, inner and outer layers 68, 70 of the barrier material 66, and a central core of the other thermoplastic material 72. Inasmuch as there is a reduction in thickness of the laminated preform on the order of ten times, the thickness of the layers 58, 60 in the bottle 128 will be on the order of .0254mm to .102mm (.001 to .004 inch), while the thickness of the barrier material layers 68,70 will be on the order of .0076 mm (.0003 inch). The thickness of the layer 58 will be sufficient to protect the barrier layer 68 against the contents of the bottle 128 including available CO^2.

Further, it has been found that when the barrier material 66 does not have properties which permit the heat bonding thereof to the thermoplastic resin and the thickness of the layers 68, 70 have been relatively great as required by known practices, when the blow molded article has been formed there has been a positive delamination of the layers of barrier material from the remainder of the blow molded article. However, when the barrier material layers in the preform are very thin, as described hereinabove, it has been found that the prior pronounced delamination does not occur. A conventional test for delamination is the squeezing of the body of a blow molded article, and if there is delamination there will be a squeaking noise emitted. When the barrier material layers are very thin at the start, the blow molded articles utilizing such a preform do not emit the squeaking noise and do not show evidence of a complete delamination.

There has recently been developed by others a five-layer tubular parison which is formed as an extruded tube. Such parison does have a barrier layer which is thin, but which is not directly bonded to the thermoplastic resins which form the primary layers of the parison. The method of forming such a multi-layer parison is not conducive to The diffusion bonding of a barrier layer to a conventional thermoplastic resin layer by way of pressure when the materials of the two layers are not normally heat bondable together in that the components of such a tubular parison are extruded at a low pressure on the order of 2000 to 5000 p.s.i. and as soon as the tube leaves the extrusion head, at which time all components are hot, the pressure is relieved and as the components cool they shrink and tend to separate.

On the other hand, as is schematically shown in figure 7, when the various materials are introduced into the mold cavity 22 by a conventional injection molding process, the barrier layers 68, 70, in addition to being very thin and thus relatively incompressible, are clamped between the core 72 and the layers 58, 60 at a very high pressure on the order of 1.034×10^8 to 1.17×10^8 Pa (15,000 to 17,000 p.s.i.). Therefore, while the barrier layers 68,70 may not be heat bondable to the thermoplastic resin layers 58, 60 and the core 72, there is a considerable diffusion bonding effected between these layers at the high forming temperatures and pressures. Further, as is also shown in Figure 7, after the injection step has been completed there is a maintaining of a high pressure on the materials previously injected into the mold cavity and thus the pressure is maintained between the layers as the materials of the layers shrink, thereby preventing any tendency to separate due to relative shrinkage.

Since the thickness of the barrier layers 68, 70 may be as low as .076mm (.003 inch), it will be apparent that it is of a relatively incompressible thinness. Further, as disclosed hereinbefore, the

preform at least in the body portion of the resultant blow molded hollow member, will be steetched on the order of ten times, thereby reducing the thickness of the barrier layers 68, 70 to be as low as .0076mm (.0003 inch), which thinness results in the resultant barrier layers as being extremely thin and thus incompressible for all practical purposes. The net result is that in the resultant blow molded hollow member the barrier layers 68, 70 maintain a pressure bond with the thermoplastic resin layers 58, 60 and the core 72.

Although specific materials have been described as being beneficially acceptable, it is to be understood that the possibilities of utilizing barrier materials which are not commercially acceptable at this time definitely exist because of the ability to maintain the thickness of the barrier material layers in the blow molded article one which provides for the desired barrier characteristics without utilization of an excess amount of the otherwise prohibitively expensive material.

Alhtough only several preferred embodiments of the invention, which is defined by the claims, have been specifically illustrated and described herein, it is to be understood that material layers within the preforms may be varied in accordance with the desired uses of the preforms and the resultant blow molded articles.

Claims

1. A method of forming a laminated preform of the type including an intermediate barrier layer, the method comprising the steps of:

   providing an injection mold (20) for said preform wherein the injection mold (20) includes a core (24) with there being a cavity (22) surrounding the core,

   providing separate supplies of at least one first flowable thermoplastic resin (56, 72) adapted to form the skin of the preform and a second flowable material (66),

   injecting into that end of said mold cavity which defines a preform bottom a limited quantity of said first thermoplastic resin (56) with the surface portions of said limited quantity of thermoplastic resin coming into contact with said mold (20) and said core (26),

   injecting a limited quantity of said second material (66) into said mold cavity behind said limited quantity of first thermoplastic resin for forming said at least one intermediate layer with said second material forcing said first thermoplastic resin further into said cavity with said second material having tunnel flow within said thermoplastic resin with surface portions of said second material in contact with said first thermoplastic resin,

   and then injecting other flowable thermoplastic resin (72) into said mold cavity (22) behind said second material (66) sufficient to complete filling of said mold cavity with said other flowable thermoplastic resin forcing said limited quantities of said first thermoplastic resin (56) and said second material (66) to flow toward the other end of said mold cavity (22), and permitting all of the injected material to solidify, characterised in that said second flowable material (66) is a barrier material, in that the surface portions of said limited quantity of thermoplastic resin cool due to contact with said mold (20) and said core (26) to define first solidified layers (58, 60) while there is tunnel flow of the thermoplastic resin between said solidified layers, in that surface portions of said second, barrier material in contact with said first thermoplastic resin cool and form second solidified layers (68, 70), and wherein said barrier material (66) has a melting temperature lower than that of said other thermoplastic resin (72) with said other thermoplastic resin as it flows between the layers (68, 70) of barrier material heating contacted layers of said barrier material and forcing portions thereof forwardly into said mold cavity (22) thereby to effect thinning of the layers of barrier material.

2. A method according to claim 1 wherein the combined thickness of the barrier material layers (68, 70) is as low as 0.153mm (0.006 inch).

3. A method according to claim 1 or 2 wherein the injected quantity of the barrier material (66) is insufficient for the barrier layers (68, 70) to extend the full length of said mold cavity (26).

4. A method according to claim 3 wherein said barrier layers (68, 70) terminate internally of the resultant preform between said layers of thermoplastic resin and said other thermoplastic.

5. A method according to any of claims 1 to 4 wherein the injected limited quantity of said thermoplastic material (56) is sufficient for the first solidified layers (58, 60) to extend the full length of said mold cavity.

6. A method according to any of claims 1 to 5 wherein said quantity of thermoplastic resin

(56) and said other thermoplastic resin (72) are provided from a common source.

7. A method according to any of claims 1 to 6 wherein said barrier material (66) has a melting temperature lower than that of said quantity of thermoplastic resin (56, 72).

8. A method according to any of claims 1 to 7 wherein the thickness of said first solidified layers (58, 60) is at least in part controlled by controlling the temperature of said core (26) and said injection mold (20) and thus the rate of cooling of said thermoplastic resin (56) forming said first solidified layers.

9. A method according to claim 8 wherein the thickness of said first solidified layers (58, 60), is at least in part controlled by the temperature of the injected thermoplastic resin (56) forming said first solidified layers.

10. A method according to any of claims 1 to 9 wherein the thickness of said solidified layers (68, 70) of said barrier material (66) is at least in part controlled by the temperature of said first solidified layers (58, 60) and thus the rate of cooling of said barrier material.

11. A method according to claim 10 wherein the thickness of said solidified layers (68, 70) of said barrier material (66) is at least in part controlled by the temperature of the injected barrier material.

12. A method according to claim 10 or 11 wherein the thickness of said solidified layers (68, 70) of said barrier material (66) is at least in part controlled by the injected other thermoplastic resin (72).

Revendications

1. Méthode de formation d'une préforme stratifiée du type comprenant une couche de barrage intermédiaire, la méthode comprenant les étapes de :

prévoir un moule (20) pour injection pour ladite préforme, dans laquelle le moule (20) pour injection comprend une partie centrale (24), une cavité (22) entourant la partie centrale,

prévoir des amenées séparées d'au moins une première résine thermoplastique (56, 72) apte à l'écoulement adaptée pour former la peau de la préforme et une deuxième matière (66) apte à l'écoulement,

injecter dans l'extrémité de ladite cavité du moule qui définit un fond de préforme une quantité limitée de ladite première résine thermoplastique (56), les parties de surface de ladite quantité limitée de résine thermoplastique venant en contact avec ledit moule (20) et ladite partie centrale (26),

injecter une quantité limitée de ladite deuxième matière (66) dans ladite cavité du moule derrière ladite quantité limitée de première résine thermoplastique pour former au moins une dite couche intermédiaire, ladite deuxième matière forçant ladite première résine thermoplastique plus loin dans la cavité, ladite deuxième matière ayant un écoulement en tunnel au sein de ladite résine thermoplastique avec les parties de surface de ladite deuxième matière en contact avec ladite première résine thermoplastique,

et ensuite injecter une autre résine thermoplastique (72) apte à l'écoulement dans ladite cavité (22) du moule derrière ladite deuxième matière (66) en quantité suffisante pour finir de remplir ladite cavité du moule, l'autre résine thermoplastique apte à l'écoulement forçant lesdites quantités limitées de ladite première résine thermoplastique (56) et de ladite deuxième matière (66) à s'écouler vers l'autre extrémité de ladite cavité (22) du moule, et permettant à toute la matière injectée de se solidifier, caractérisée en ce que ladite deuxième matière (66) apte à l'écoulement est une matière de barrage, en ce que les parties de surface de ladite quantité limitée de résine thermoplastique refroidissent à cause du contact avec ledit moule (20) et ladite partie centrale (26) pour définir des premières couches solidifiées (58, 60) alors qu'il y a un écoulement en tunnel de la résine thermoplastique entre lesdites couches solidifiées, en ce que les parties de surface de ladite deuxième matière de barrage en contact avec ladite première résine thermoplastique refroidissent et forment des secondes couches solidifiées (68, 70), et dans laquelle ladite matière de barrage (66) a un point de fusion inférieur à celui de ladite autre résine thermoplastique (72), l'autre résine thermoplastique chauffant les couches de contact de la matière de barrage alors qu'elle s'écoule entre les couches (68, 70) de ladite matière de barrage et forçant des parties de celle-là vers l'avant dans ladite cavité (22) du moule pour effectuer par là-même l'amincissement des couches de matière de barrage.

2. Méthode selon la revendication 1, dans laquelle l'épaisseur combinée des couches (68, 70) de matière de barrage est aussi faible que 0,153mm (0,006 pouce).

3. Méthode selon la revendication 1 ou 2, dans laquelle la quantité injectée de la matière de barrage (66) est insuffisante pour que les couches de barrage (68, 70) puissent s'étendre de toute la longueur de ladite cavité (26) du moule.

4. Méthode selon la revendication 3, dans laquelle lesdites couches de barrage (68, 70) finissent à l'intérieur de la préforme résultante entre lesdites couches de résine thermoplastique et ladite autre matière thermoplastique.

5. Méthode selon l'une quelconque des revendications 1 à 4, dans laquelle la quantité limitée injectée de ladite matière thermoplastique (56) est suffisante pour que les premières couches solidifiées (58, 60) puissent s'étendre de toute la longueur de ladite cavité du moule.

6. Méthode selon l'une quelconque des revendications 1 à 5, dans laquelle ladite quantité de résine thermoplastique (56) et ladite autre résine thermoplastique (72) sont fournies en provenance d'une source commune.

7. Méthode selon l'une quelconque des revendications 1 à 6, dans laquelle ladite matière de barrage (66) a un point de fusion inférieur à celui de ladite quantité de résine thermoplastique (56, 72).

8. Méthode selon l'une quelconque des revendications 1 à 7, dans laquelle l'épaisseur desdites premières couches solidifiées (58, 60) est au moins en partie régulée en régulant la température de ladite partie centrale (26) et dudit moule (20) pour injection et ainsi la vitesse de refroidissement de ladite résine thermoplastique (56) formant lesdites premières couches solidifiées.

9. Méthode selon la revendication 8, dans laquelle l'épaisseur desdites premières couches solidifiées (58, 60) est au moins en partie régulée par la température de la résine thermoplastique (56) injectée formant lesdites premières couches solidifiées.

10. Méthode selon l'une quelconque des revendications 1 à 9, dans laquelle l'épaisseur desdites couches solidifiées (68, 70) de ladite matière de barrage (66) est au moins en partie régulée par la température desdites premières couches solidifiées (58, 60) et ainsi par la vitesse de refroidissement de ladite matière de barrage.

11. Méthode selon la revendication 10, dans laquelle l'épaisseur desdites couches solidifiées (68, 70) de ladite matière de barrage (66) est au moins en partie régulée par la température de la matière de barrage injectée.

12. Méthode selon la revendication 10 ou 11, dans laquelle l'épaisseur desdites couches solidifiées (68, 70) de ladite matière de barrage (66) est au moins en partie régulée par l'autre résine thermoplastique (72) injectée.

Patentansprüche

1. Verfahren zum Bilden eines geschichteten Vorformlings von der eine Zwischensperrschicht umfassenden Art, wobei das Verfahren die folgenden Schritte umfaßt:

Vorsehen einer Spritzgußform (20) für den Vorformling, wobei die Spritzgußform (20) einen Kern (24) umfaßt und der Kern von einem Hohlraum (22) umgeben ist,

Vorsehen separater Bestände von mindestens einem ersten fließfähigen thermoplastischen Harz (56, 72), welches die Haut des Vorformlings bilden kann, und einem zweiten fließfähigen Material (66),

Spritzen einer begrenzten Menge des ersten thermoplastischen Harzes (56) in das Ende des Formhohlraums, welches einen Vorformlingsboden bildet, wobei die Oberflächenanteile der begrenzten Menge des thermoplastischen Harzes mit der Form (20) und dem Kern (26) in Berührung kommen,

Spritzen einer begrenzten Menge des zweiten Materials (66) in den Formhohlraum, und zwar hinter der begrenzten Menge des ersten thermoplastischen Harzes, zur Bildung der mindestens einen Zwischenschicht, wobei das zweite Material das erste thermoplastische Harz weiter in den Hohlraum drängt und das zweite Material einen Tunnelfluß innerhalb des thermoplastischen Harzes vornimmt, wobei die Oberflächenanteile des zweiten Materials mit dem ersten thermoplastischen Harz in Berührung stehen,

und danach Spritzen von anderem fließfähigem thermoplastischem Harz (72) in den Formhohl-

raum (22), und zwar hinter dem zweiten Material (66) und ausreichend, um den Formhohlraum vollständig auszufüllen, wobei das andere fließfähige thermoplastische Harz die begrenzte Menge des ersten thermoplastischen Harzes (56) und des zweiten Materials (66) dazu zwingt, dem anderen Ende des Formhohlraums (22) zuzufließen, und wobei die Erstarrung des gesamten gespritzten Materials ermöglicht wird, dadurch gekennzeichnet, daß das zweite fließfähige Material (66) ein Sperrmaterial ist, daß die Oberflächenanteile der begrenzten Menge thermoplastischen Harzes aufgrund der Berührung mit der Form (20) und dem Kern (26) abkühlen, um erste erstarrte Schichten (58, 60) zu bilden, während ein Tunnelfluß des thermoplastischen Harzes zwischen den erstarrten Schichten stattfindet, daß Oberflächenanteile des zweiten Sperrmaterials in Berührung mit dem ersten thermoplastischen Harz abkühlen und zweite erstarrte Schichten (68, 70) bilden, und wobei das Sperrmaterial (66) einen niedrigeren Schmelzpunkt als das andere thermoplastische Harz (72) aufweist, wobei das andere thermoplastische Harz beim Fließen zwischen den Schichten (68, 70) des Sperrmaterials berührte Schichten des Sperrmaterials erwärmt und Abschnitte desselben nach vorne in den Formhohlraum (22) drängt, um dadurch ein Verringern der Dicke der Schichten des Sperrmaterials zu bewirken.

2. Verfahren nach Anspruch 1, wobei die Gesamtdicke der Schichten (68, 70) des Sperrmaterials nur 0,153 mm (0,006 Inch) beträgt.

3. Verfahren nach Anspruch 1 oder 2, wobei die eingespritzte Menge des Sperrmaterials (66) für ein Sicherstrecken der Sperrschichten (68, 70) über die volle Länge des Formhohlraums (26) nicht ausreichend ist.

4. Verfahren nach Anspruch 3, wobei die Sperrschichten (68, 70) innerhalb des entstandenen Vorformlings zwischen den Schichten aus thermoplastischem Harz und dem anderen thermoplastischen Stoff enden.

5. Verfahren nach einem der Ansprüche 1 bis 4, wobei die eingespritzte begrenzte Menge des thermoplastischen Materials (56) für ein Sicherstrecken der ersten erstarrten Schichten (58, 60) über die volle Länge des Formhohlraums ausreichend ist.

6. Verfahren nach einem der Ansprüche 1 bis 5, wobei die Menge des thermoplastischen Harzes (56) und das andere thermoplastische Harz (72) aus einer gemeinsamen Quelle bereitgestellt werden.

7. Verfahren nach einem der Ansprüche 1 bis 6, wobei das Sperrmaterial (66) einen niedrigeren Schmelzpunkt als die Menge des thermoplastischen Harzes (56, 72) aufweist.

8. Verfahren nach einem der Ansprüche 1 bis 7, wobei die Dicke der ersten erstarrten Schichten (58, 60) zumindest teilweise durch die Regelung der Temperatur des Kerns (26) und der Spritzgußform (20), und somit der Abkühlgeschwindigkeit des die ersten erstarrten Schichten bildenden thermoplastischen Harzes (56) geregelt wird.

9. Verfahren nach Anspruch 8, wobei die Dicke der ersten erstarrten Schichten (58, 60) zumindest teilweise von der Temperatur des die ersten erstarrten Schichten bildenden gespritzten thermoplastischen Harzes (56) geregelt wird.

10. Verfahren nach einem der Ansprüche 1 bis 9, wobei die Dicke der erstarrten Schichten (68, 70) des Sperrmaterials (66) zumindest teilweise durch die Temperatur der ersten erstarrten Schichten (58, 60) und somit der Abkühlgeschwindigkeit des Sperrmaterials geregelt wird.

11. Verfahren nach Anspruch 10, wobei die Dicke der erstarrten Schichten (68, 70) des Sperrmaterials (66) zumindest teilweise durch die Temperatur des gespritzten Sperrmaterials geregelt wird.

12. Verfahren nach Anspruch 10 bzw. 11, wobei die Dicke der erstarrten Schichten (68, 70) des Sperrmaterials (66) zumindest teilweise durch das gespritzte andere thermoplastische Harz (72) geregelt wird.

FIG.1

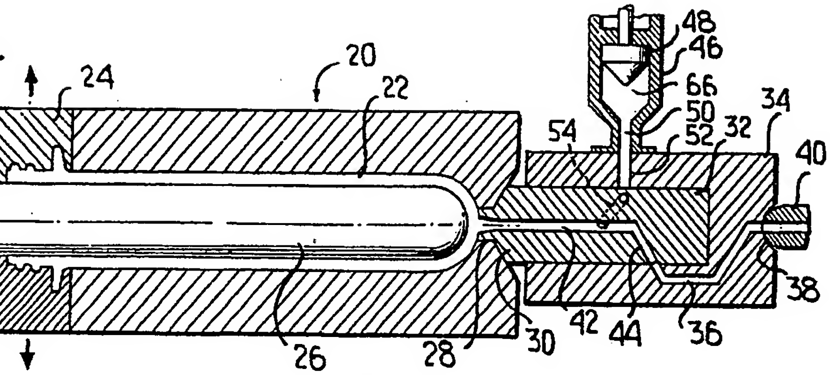

FIG.2

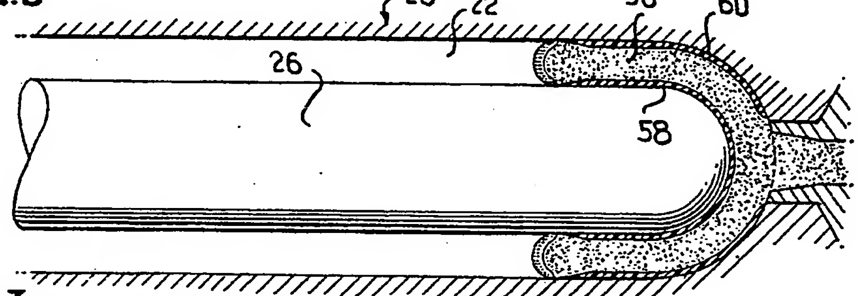

FIG.3

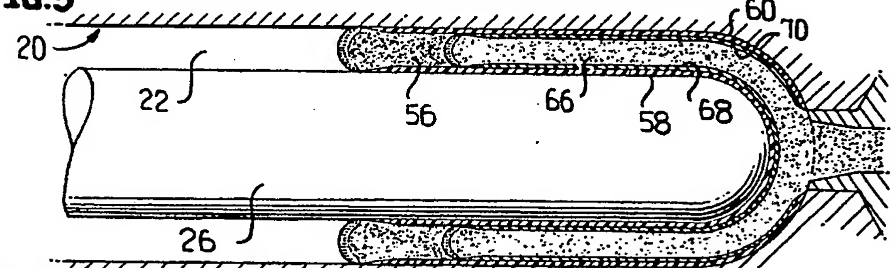

FIG.4

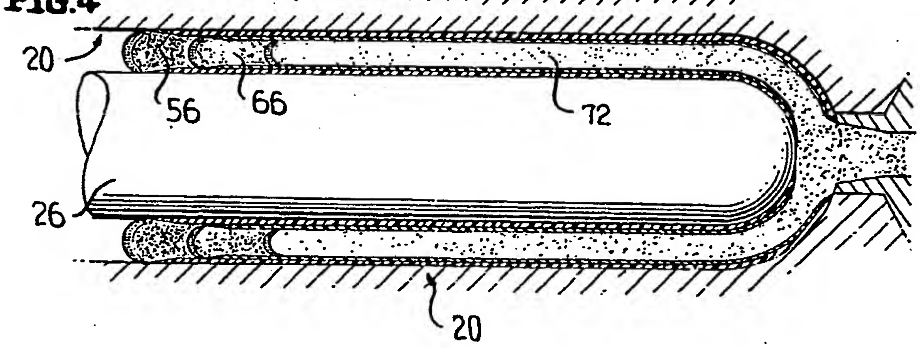

FIG.5

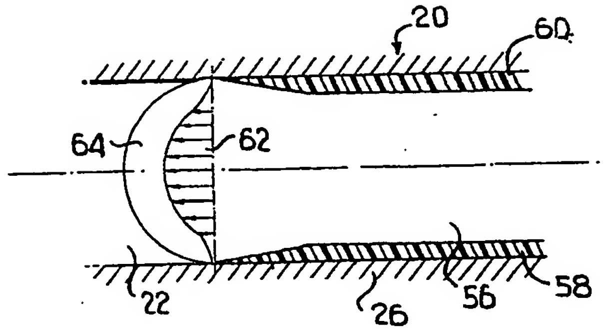

FIG.6

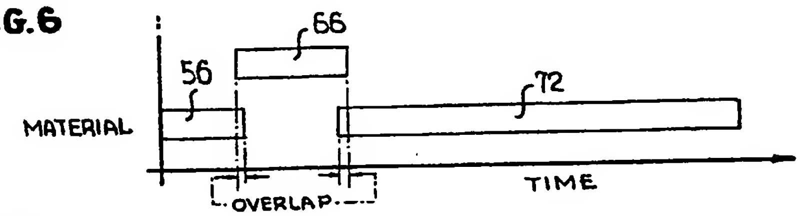

FIG.8

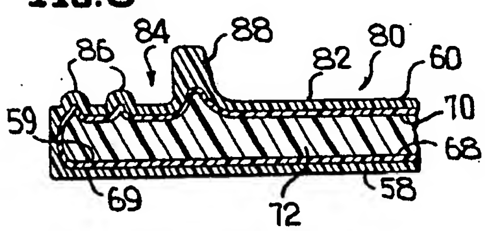

FIG.9

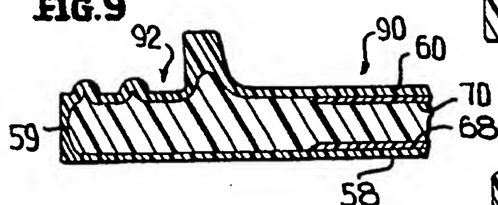

FIG.10

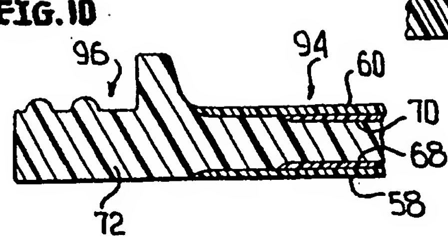

FIG.11

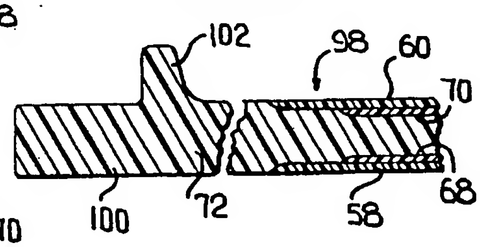

FIG.12

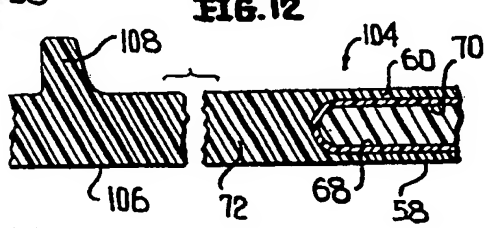

FIG.13

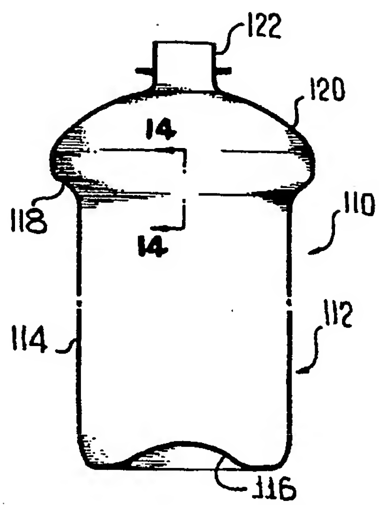

FIG.14

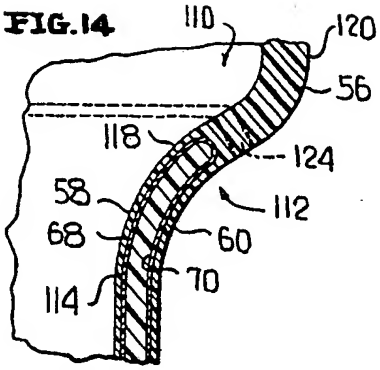

FIG.15

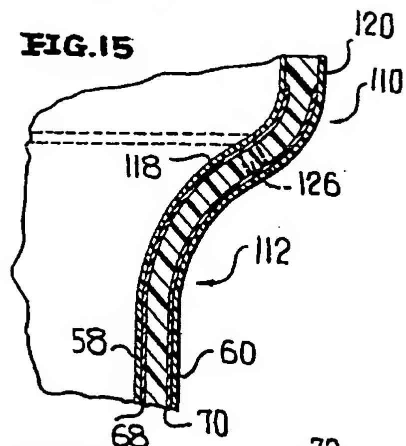

FIG.16

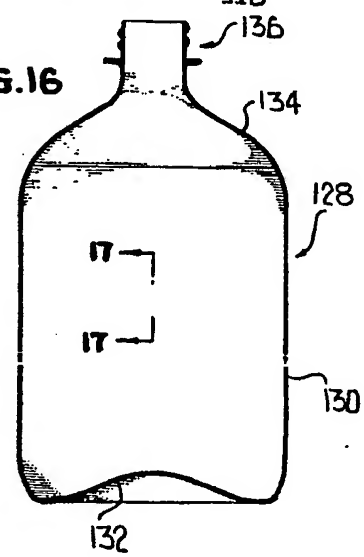

FIG.17

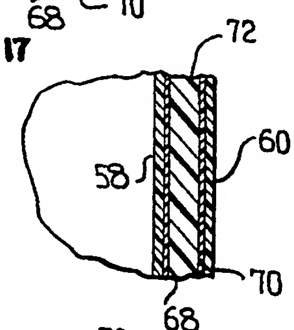

FIG. 7